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(56) Documents considered for evaluation of patentability:

DE 31 26 110 A1
GB 21 45 079 A
EP 01 71 009 A2
WO 96 14 311
Chem. Abstr. 68 (1968), Ref. 14298
Fat Sci. Technol. 91 (1989), pp. 39-41
JAOCS 73/10 (1996), pp. 1271-1274

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(54) [Title of the Invention]: **Method for the Concentration of Tocopherols and Sterols**

(57) [Abstract]

The object of the present invention is a method for the concentration of tocopherols and/or sterols from tocopherol- and/or sterol-containing mixtures of fats and/or fat derivatives in which the mixtures are subjected directly to fractional distillation and molecular distillation. Evaporator distillates, especially soybean oil, rapeseed oil or sunflower oil evaporator distillates are preferably used for the concentration process. The method can also be conducted in a temporal succession in a correspondingly designed apparatus. If the fatty acid is divided into a distillate and side stream, higher grade fatty acid can be recovered.

Description

Introduction

The invention relates to a method for the concentration of tocopherols and/or sterols from tocopherol and/or sterol-containing mixtures of fats and/or fat derivatives in which the mixtures are directly subjected to fractional distillation and molecular distillation, i.e., without prior reaction or addition of auxiliaries.

Prior Art

Tocopherol compounds are contained in many vegetable oils and animal fats and are also referred to as vitamin E. The designation vitamin E refers to the physiological effect of these food ingredients.

Eight naturally occurring substances with a vitamin E effect are known. They are derivatives of 6-chromanol and belong to two groups of compounds. The first group is derived from tocol and carries a saturated isoprenoid side chain with 16 carbon atoms. This group includes α -, β -, γ - and δ -tocopherol. The compounds differ in degree of methylation on the benzene ring of the tocol. α -Tocopherol is the substance with the strongest biological vitamin E effect and has the greatest technical and economic significance. It is the dominating tocopherol in human and animal tissue.

The second group of substances with vitamin E effect constitutes derivatives of tocotrienol. They differ from the other tocopherol homologs on account of the unsaturated isoprenoid side chain with 16 carbon atoms. The naturally occurring tocoenols also exhibit a vitamin E effect and are ordinarily isolated together with saturated tocopherol homologs from their natural sources during preparation of vitamin E. The term "tocopherol" in this application is also supposed to include these tocopherol homologs, i.e., all substances with a vitamin E effect.

Because of their oxidation-inhibiting (*anti-oxidant – translator*) properties, tocopherols find application in the food and cosmetic-pharmaceutical branch, and as additives in paints based on natural oils.

The term "sterol" in this application includes the sterols, which are also called sterins. Both terms "sterol" and "sterin" are used as equivalent in this patent application. The sterols are

monohydric secondary steroid alcohols with 27 to 30 carbon atoms having the basic structure of gonane. Carbon atom 3 of gonane carries the hydroxyl group. The structural differences of the individual sterols thus far found in nature consist of the occurrence of double bonds within a ring system, entry of substituents at preferred sites and the constitution of the side chain, which is anchored on carbon atom 17 of gonane.

The most important representative of sterols is cholesterol, which occurs freely or esterified in animal organs and fluids, especially in the brain, spine, adrenal glands, in cod liver oil and wool grease. Cholesterol belongs to the so-called zoosterols, a term used to denote the sterols contained in animals fats. The plant sterols are called phytosterols. The most important representatives are ergosterol, stigmasterol, campesterol and sitosterol. The sterins or sterols are valuable starting substances in the synthesis of drugs, especially steroid hormones, for example, corticosteroids and gestagens. For example, stigmasterol can be easily converted to progesterone.

The initial mixtures for the production of tocopherol and sterol can be a number of plant and animal substances. The highest concentrations of tocopherol are found in vegetable oils like wheat germ, corn, soybean and palm kernel oil. Tocopherol, however, is also found in other vegetable oils, for example safflower oil, peanut oil, cottonseed oil, sunflower oil, rapeseed oil, palm oil and other vegetable oils.

The natural vegetable oils contain only limited amounts of tocopherol. An increased concentration is desired for commercial applications. Contaminants should also be removed in order to reinforce the antioxidant effect and vitamin E activity. The most important natural sources for tocopherol are therefore not the vegetable oils themselves, but the steam distillates that form during deodorization of vegetable oils and animals fats, which are also called evaporator distillates. The tocopherols are concentrated in this case but mixed with sterol and sterol esters, free fatty acids, as well as triglycerides. The distillates from deodorization of soybean oil, rapeseed oil and sunflower oil are of particular interest. The particular suitability of soybean oil as a source of tocopherol is mentioned, for example, in *Fat Sci. Technol.* **91**, 1989, pp. 39-41 in a comparison of deodorization distillates of soybean and rapeseed oils. Depending on the deodorization process, the distillates contain between 1 and 10 % by weight mixed tocopherols and sterols in equal amounts, which are mostly present in their ester form.

Different methods alone or in combination are known for the concentration of tocopherol, namely esterification, saponification, fractional extraction and distillation. Tocopherol concentrates are recovered according to DE 31 26 110 A1 from the byproducts of the deodorization of oils and fats by means of esterifying the free fatty acids contained in them as a result of the addition of an alcohol or distilling off the free fatty acids from the distillates, whereupon these products are subjected to hydrogenation and then solvent fractionation to extract the tocopherols. Another method for the concentration of tocopherol is known from the same document. The deodorization distillates here are subjected to transesterification with methanol and the fatty acid methyl ester distilled off. The residue is concentrated with the help of molecular distillation.

Another method known from EP 171 009 A2 brings the tocopherol-containing material in contact with a sufficient amount of a polar organic solvent, which dissolves the tocopherols, but not the contaminants. The polar phase enriched with tocopherol is separated and the tocopherol recovered from this.

The separation of tocopherols in response to an adsorption on basic anion exchangers is also known. This variant is possible if the mixture contains no or only little fatty acids. The sterols, glycerides and other neutral or basic substances are not adsorbed (Ullmann's Encyclopedia of Industrial Chemistry, 4th edition, Vol. 23, 1984, p. 645).

GB 2 145 079 A describes in an example the use of acid ion exchangers as a catalyst for the esterification of free fatty acids contained in rapeseed oil distillate with 5 volume parts of methanol in reference to 1 volume part of deodorization distillate. Since ingredients insoluble in methanol precipitate, esterification is conducted in a fluidized bed. The need for a fluidized bed leads to a costly process, whose economic efficiency is doubtful in an industrial setting.

Fractional crystallization is also known for the separation of sterols from tocopherols after concentration. In this case, the tocopherol enters solution and the sterol crystallizes out. A distillative separation of tocopherol and sterol is also possible, but in this case the sterol is at least partly destroyed.

Even recently, there has been no decline in efforts to find better methods for the production of tocopherols. It is pointed out in an article of Gosh and Bhattacharyya (JAOCS, Vol. 73, No. 10, 1996) that there is a demand for new processes to produce tocopherols and sterols. A method is proposed in this article, in which, starting from soybean oil evaporator

distillate, enzymatic hydrolysis is initially conducted, followed by the esterification of the free fatty acids (also enzymatically) and finally concentration of tocopherols and sterols by means of fractional distillation. 70 % by weight of the tocopherol in reference to the evaporator distillate could be obtained by means of this rather costly method.

A feature common to all known methods is that they are generally quite expensive. High costs are incurred during separation of the fatty acid components that are of limited value from an economic standpoint, but which account for the largest weight fraction of the evaporator distillate. Molecular distillation is a less demanding method that gets by without a reaction step or other auxiliaries, like solvents.

A method based on molecular distillation is presented as the most efficient method by Kim and Rhee (Korean J. Food Sci. Technol., Vol. 14, No. 2, 1982) by comparison of different methods for the recovery of tocopherol and sterol. In the case of this method, the evaporator distillate is directly subjected to molecular distillation without prior workup – only degassing of the material is advisable. During this first molecular distillation, however, 15 % by weight of the tocopherols and 10 % by weight of the sterols are separated with the free fatty acids. A second molecular distillation then occurs and the tocopherols are obtained in a yield of about 70 % by weight and the sterols in a yield of about 60 % by weight, in reference to the employed evaporator distillate. A significant drawback of this method, naturally, is represented by the high tocopherol losses. This is of special significance, because the value of the tocopherol contained in the evaporator distillate exceeds the value of all the other components several-fold and therefore determines the raw material price. The amounts of available evaporator distillates cannot be arbitrarily increased either, since they only occur as an adjunct product of edible oil production.

The complex task of the present invention therefore was to provide a method for the concentration of tocopherols and sterols, starting from tocopherol and/or sterol-containing mixtures of fats and/or fat derivatives, which can be easily conducted industrially and gets by with few process steps but at the same time minimizes losses of tocopherol during workup. The method should also permit steam distillates with a tocopherol content below 3 % by weight to be worked up in high yields.

Description of the Invention

The object of the invention therefore is a method for the concentration of tocopherols and/or sterols, starting from tocopherol and/or sterol containing mixtures of fats and/or fat derivatives in which the mixtures are directly subjected to fractional distillation and molecular distillation.

It has now surprisingly been found that as a result of using fractional distillation for the separation of the free fatty acids, the high tocopherol losses known from the prior art can be avoided. More than 90% of the tocopherol and/or 80% of the free sterol can be concentrated from the mixtures of fats and/or fat derivatives by means of only a two-stage process.

Fats and Fat Derivatives

A number of different mixtures containing tocopherol and sterol are suitable as starting material for the method underlying the invention. It is particularly advantageous, if one starts from soybean oil, rapeseed oil or sunflower oil evaporator distillate. This is obtained by means of a steam distillation of the crude oil as a first stage of the deodorization process. The distillate contains up to 20% sterol, 8% tocopherol, 20% free fatty acid and triglycerides as the main component (Ullmann, loc. cit.)

However, the method is not restricted to evaporator distillates of vegetable oils and fats. Tall oil can also be used to advantage. Tall oil is one of the most economically important byproducts of the cellulose-sulfate method of papermaking. It is obtained as a result of the acidification of the sodium salt mixture of resin and fatty acids occurring in this method. Tall oil is a natural mixture of resin acids of the abietic acid type, saturated and unsaturated fatty acids, as well as fatty acid esters and nonsaponifiables. The nonsaponifiables also contain sterols, in addition to higher alcohols and hydrocarbons.

Other tocopherol-containing mixtures can also be worked up with the method according to the invention, for example, the residue occurring during rapeseed oil-methyl ester production, which also contains sterols and sterol esters.

Fractional Distillation

Fractional distillation is conducted according to the method known from the prior art. For this purpose, a distillation column equipped with a high performance fabric packing (for example Sulzer BX) is preferably used. A wiped thin film evaporator with a single pass of the product is preferably used as bottom evaporator. The use of a falling film evaporator with minimized holdup is also possible as an alternative (for example K. Sattler, *Thermal Separation Methods*, VCH Publishers, Weinheim, 1988, pp. 503-507). Minimization of the thermal load on the material is essential to achieve high yields. In order to guarantee the most complete possible retention of tocopherol and sterol in the bottoms with simultaneous fullest possible separation of the free fatty acids and other low-boiling components in comparison with tocopherol, columns with three to 10, especially five theoretical separation stages are preferably used. Packing lengths of at least 1, especially at least 2 m, are preferred. On the other hand, the packing must not be too long so that the bottom pressure and therefore the bottom temperature do not rise too sharply. Fractional distillation is typically run at an overhead pressure of 0.5 to 10, preferably 1 to 6 mbar, at a bottom pressure of 1 to 30, especially 5 to 10 mbar and at bottom temperatures between 200 and 350, especially 250 and 300°C.

In another preferred embodiment, this distillation column can have a side takeoff so that a fatty acid fraction can be taken off as side stream, thus producing a higher grade fatty acid. In the context of fractional distillation, the free fatty acids and other low-boiling components are removed from the mixture without simultaneously removing tocopherols and/or sterols.

Molecular Distillation

In a second process step, the bottoms from the fractional distillation are subjected to molecular distillation. Tocopherol and free, i.e., nonesterified sterol are distilled from the high-boiling components of the evaporator distillate, for example, triglycerides. A wiped thin film evaporator is preferably used in this case, which has an integrated condenser (K. Sattler, loc. cit., pp. 118-120). A sufficiently small distillation pressure can be reached, so that tocopherol and free sterol can be distilled off without excess thermal load. A typical pressure in this step is 10^{-2} to 3, preferably 10^{-2} to $2 \cdot 10^{-1}$ mbar. The temperatures again lie between 200 and 350°C, especially 250 and 300°C.

Both process steps can also be conducted in succession in an installation, when the evaporator for the molecular distillation is used as the bottom evaporator for the column. In this type of operation, the integrated condenser of the evaporator is not used during fractional distillation. For the second step the vacuum system must be directly connected to the evaporator, bypassing the column through a vapor tube, for example.

If the amount of free fatty acids and other relatively low-boiling components is very small in comparison with the amount of high-boiling components, it can also be advantageous to reverse the sequence of steps. In this case free fatty acids, tocopherol, free sterol and other low-boiling components are distilled off in a molecular distillation from the high-boiling components, like triglycerides. This distillate is then subjected to the aforementioned fractionation, during which the tocopherol-sterol concentrate occurs as bottom product.

Examples

Example 1

Evaporator distillate from soybean oil refining was fractionated in a pilot column (diameter 70 mm) packed with a textured fabric packing 1 m long and a wiped thin film evaporator (0.065 m²). The overhead pressure of the column was 6 mbar. The temperature of the heating medium was 280°C. The starting material had a tocopherol concentration of 6.2% and a free sterol concentration of 6.9%. The acid number was 93. 51% of the charge was separated as distillate. No tocopherol and 0.1% sterol were found in the distillate. The acid number of the distillate was 168. The concentration in the bottom product was 13.9% tocopherol and 11.9% sterol. The acid number of the bottom product was 13. The bottom product was subjected to molecular distillation at a pressure of 0.08 mbar and a heating agent temperature of 280°C. 60% of the charge for molecular distillation was taken off as distillate (= evaporator distillate concentrate). The concentrate had a tocopherol concentration of 24.9% and a sterol concentration of 20.3%. Only traces of tocopherol (0.2%) and free sterol (0.3%) were found in the residue. A tocopherol yield of the entire process was nominally above 100%, the free sterol yield was 85%.

Example 2

Evaporator distillate from rapeseed oil refining was subjected to molecular distillation at a pressure of 0.07 mbar and a heating agent temperature of 290°C. The starting material had a tocopherol concentration of 3.3% and a free sterol concentration of 2.8%. 77% of the charge for molecular distillation was taken off as distillate. The distillate had a tocopherol concentration of 4.5% and a sterol concentration of 3.5%. The acid number was 95. Only traces of tocopherol (0.6%) and free sterol (0.5%) were found in the residue. The distillate was fractionated in a pilot column packed with a textured fabric packing and a wiped thin film evaporator. The overhead pressure of the column was 1.6 mbar. The temperature of the heating medium was 275°C. 51% of the charge was separated as distillate. Less than 0.1% tocopherol and 0.1% sterol were found in the distillate. The acid number of the distillate was 164. The concentration in the bottom product (= evaporator distillate concentrate) was 7.7% tocopherol and 5.8% sterol. The acid number of the bottom product was 27. The tocopherol yield of the entire process was nominally above 100%, the free sterol yield at 85%.

Example 3

Evaporator distillate from rapeseed oil refining was fractionated in a pilot column packed with a textured fabric packing and a wiped thin film evaporator. The overhead pressure of the column was 1.8 mbar. The temperature of the heating medium was 275°C. The starting material had a tocopherol concentration of 2.2% and a free sterol concentration of 4.0%. The acid number was 158. 9.2% of the charge was separated as distillate. 0.1% tocopherol and 0.1% sterol were found in the distillate. The acid number of the distillate was 193. 69% of the charge was taken off as side stream. No tocopherol and 0.2% sterol were found in this side stream. The acid number was 202.5, i.e., the side stream is of higher value for use as fatty acid than the corresponding streams from examples 1 and 2. The concentration in the bottom product was 10.9% tocopherol and 16.4% sterol. The acid number of the bottom product was 5.6. The bottom product was subjected to molecular distillation at a pressure of 0.15 mbar and a temperature of the heating medium of 290°C. 72% of the charge for molecular distillation was taken off as distillate (= evaporator distillate concentrate). The concentrate had a tocopherol concentration of 14.8% and a sterol concentration of 23.5%. Only traces of tocopherol (0.2%)

and free sterol (0.6%) were found in the residue. The tocopherol yield in the overall process was nominally above 100%, the free sterol yield at 88%.

Comparative Example

Evaporator distillate from soybean oil refining was subjected to an open-path distillation or deacidification at 1 mbar and 250°C. The starting material had a tocopherol concentration of 9.8% and a free sterol concentration of 8.1%. The acid number was 100. 58% of the charge was separated as distillate. 2.6% tocopherol and 0.9% sterol were found in the distillate. This corresponds to a loss of 20% of the employed tocopherol with the distillate. On the other hand, the acid number of the residue was still 35 so that deacidification was not nearly as complete as in the aforementioned examples.

Claims

1. A method for the concentration of tocopherols and/or sterols from tocopherol- and/or sterol-containing mixtures of fats and/or fat derivatives, **characterized by the fact** that the mixtures are subjected directly to fractional distillation and molecular distillation.
2. The method according to Claim 1, characterized by the fact that a wiped thin film evaporator is used as a bottom evaporator for the fractional distillation.
3. The method according to Claim 1, characterized by the fact that a falling film evaporator is used as a bottom evaporator for the fractional distillation.
4. The method according to Claims 1 to 3, characterized by the fact that evaporator distillates are used as starting substances.
5. The method according to Claims 1 to 4, characterized by the fact that rapeseed oil, sunflower oil or soybean oil evaporator distillates are used.
6. The method according to Claims 1 to 5, characterized by the fact that the fractionation is carried out first and then molecular distillation.
7. The method according to Claims 1 to 5, characterized by the fact that molecular distillation is carried out first and then fractionation.
8. The method according to Claims 1 to 7, characterized by the fact that a fatty acid fraction is taken off as side stream from the column.